



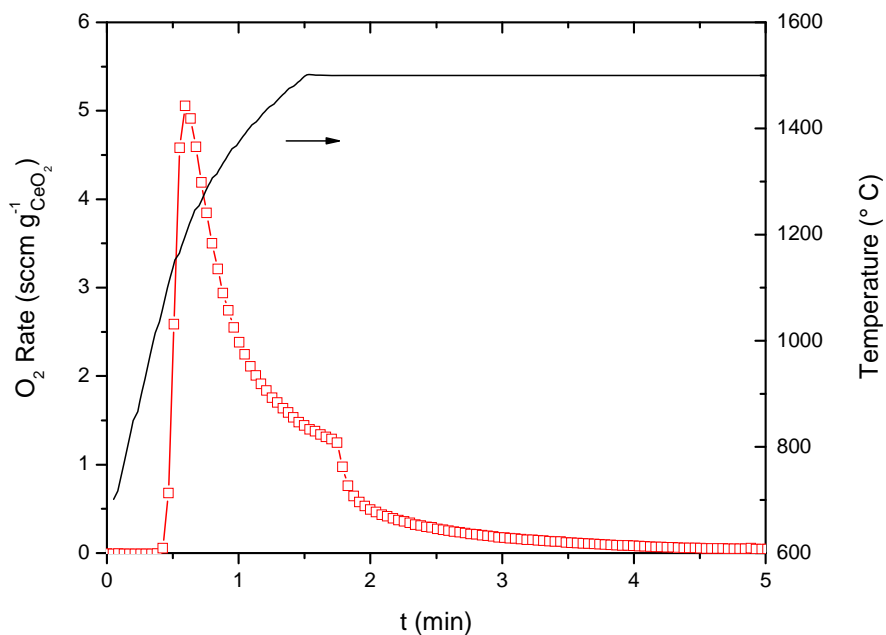
## Supporting Information

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# **Ceria as a Thermochemical Reaction Medium for Selectively Generating Syngas or Methane from H<sub>2</sub>O & CO<sub>2</sub>**

William C. Chueh, Sossina M. Haile

Supporting Information



**Fig. S1.** Oxygen release rate from fully oxidized  $\text{CeO}_2$  upon rapid heating from 700 to 1500  $^{\circ}\text{C}$  in an infrared furnace under flowing 11 ppm  $\text{O}_2$  in  $\text{N}_2$  supplied at a flow rate of 1470  $\text{sccm g}^{-1}_{\text{CeO}_2}$ . Oxygen evolution was rapid and limited by the ramp rate of the furnace. Integrating the rate curve gives an oxygen nonstoichiometry of 0.06.

The sample was fabricated in the same way as indicated in the Experimental section. An alumina tube (9.5 mm inner diameter) served as the reactor with the exhaust gas connected to a Pfeiffer Thermostar quadrupole mass spectrometer.

**Ni-SDC**

<i>Temperature</i> (°C)	$V_{H_2}$ (mL g <sup>-1</sup> )	$V_{CH_4}$ (mL g <sup>-1</sup> )	$V_{CO}$ (mL g <sup>-1</sup> )	$S_{CH_4}$ (%)	$X$
400	1.0 ± 0.1	1.1 ± 0.1	0.05 ± 0.01	80	0.8 ± 0.1
500	3.2 ± 0.3	0.7 ± 0.1	0.28 ± 0.02	46	1.0 ± 0.1
600	4.3 ± 0.3	0.30 ± 0.02	1.3 ± 0.1	18	1.1 ± 0.1
700	4.1 ± 0.3	0	1.9 ± 0.2	0.2	0.9 ± 0.1

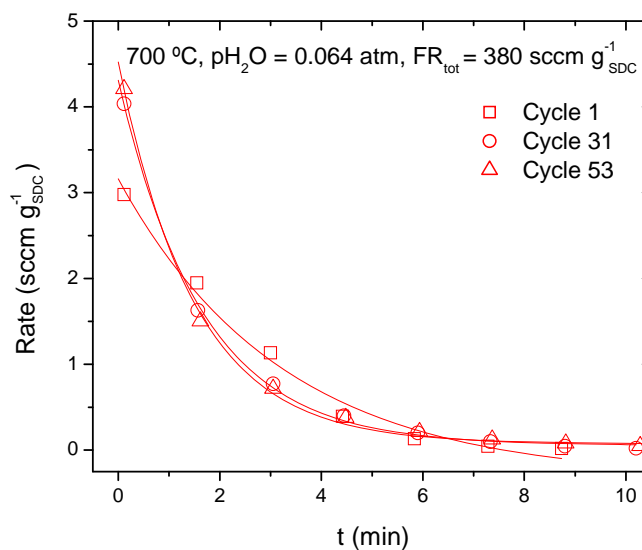
**Table S1(a).** Fuel productivity and extent of reaction data corresponding to Fig. 2(top).

**SDC**

<i>Temperature</i> (°C)	$V_{H_2}$ (mL g <sup>-1</sup> )	$V_{CH_4}$ (mL g <sup>-1</sup> )	$V_{CO}$ (mL g <sup>-1</sup> )	$S_{CH_4}$ (%)	$X$
400	4.7 ± 0.4	0	0.36 ± 0.08	0	0.8 ± 0.1
500	4.5 ± 0.4	0	1.8 ± 0.1	0	1.0 ± 0.1
600	3.9 ± 0.3	0	1.8 ± 0.1	0	0.9 ± 0.1
700	4.1 ± 0.3	0	2.0 ± 0.2	0	0.9 ± 0.1

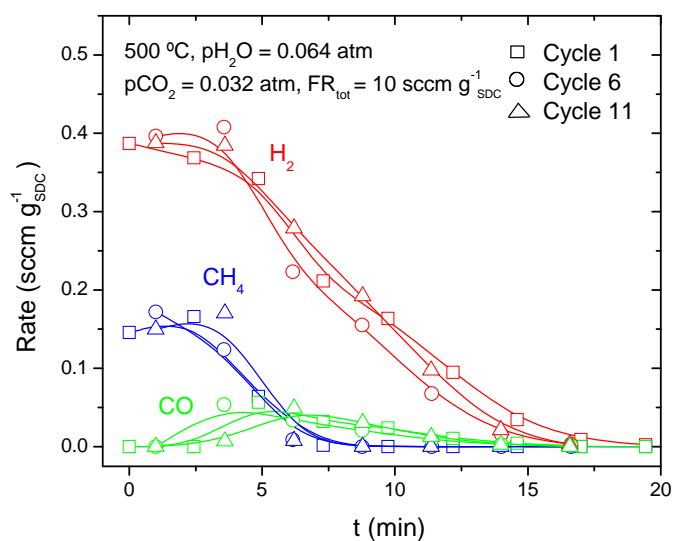
**Table S1(b).** Fuel productivity and extent of reaction data corresponding to Fig. 2(bottom)

$V$  is the total volume of gas produced,  $S_{CH_4}$  is the methane selectivity, defined as  $S_{CH_4} = 4V_{CH_4}/(4V_{CH_4} + V_{H_2} + V_{CO})$  and  $X$  is the extent of reaction, defined as the ratio of fuel produced to the theoretical fuel productivity, as set by the initial oxygen nonstoichiometry.



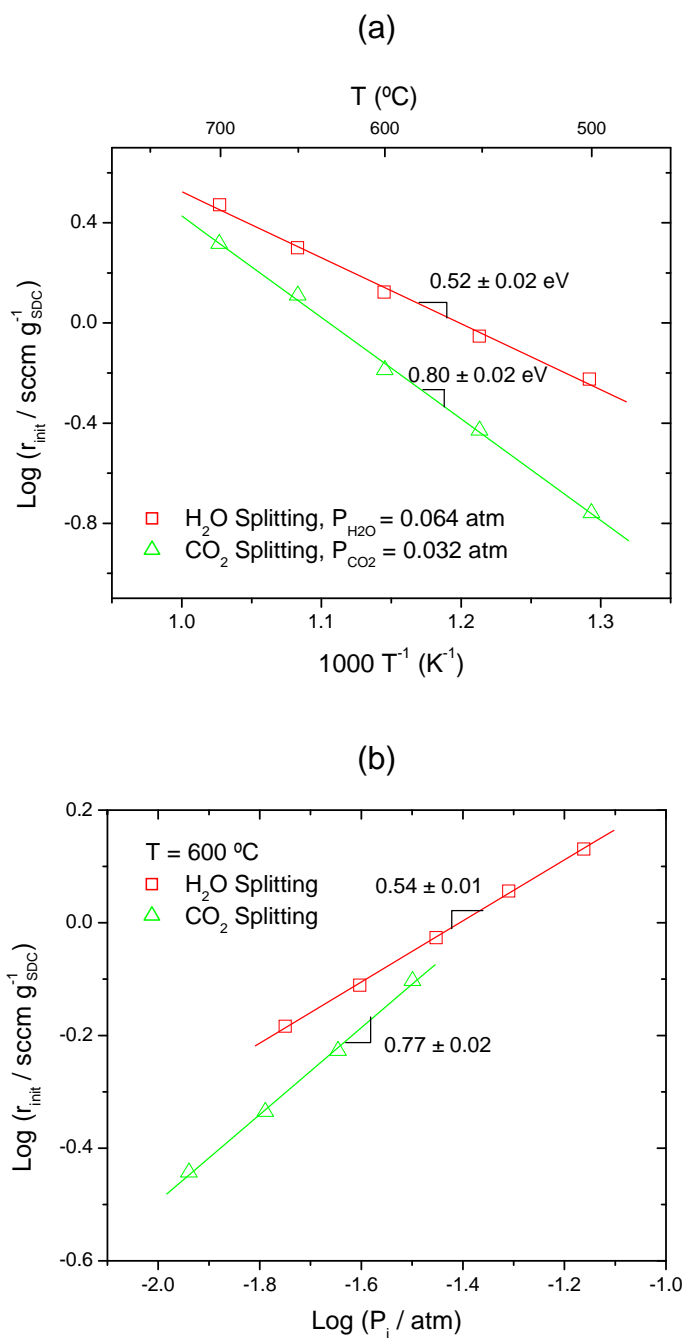
Cycle No.	$V_{H_2}$ ( $mL\ g^{-1}$ )	$X$
1	$7.6 \pm 0.6$	$1.2 \pm 0.1$
31	$7.6 \pm 0.6$	$1.2 \pm 0.1$
53	$7.7 \pm 0.6$	$1.2 \pm 0.1$

**Fig. S2 / Table S2.**  $H_2$  production as a function of time, as measured by gas chromatography upon exposure of reduced SDC to mildly humidified  $N_2/Ar$  at the conditions indicated ( $FR_{tot}$  is the total flow rate). Efficacy of  $H_2O$  splitting is largely unchanged after 53 redox cycles (other cycles at various conditions).  $V$  is the total volume of gas produced,  $S_{CH_4}$  is the methane selectivity, defined as  $S_{CH_4} = 4V_{CH_4}/(4V_{CH_4} + V_{H_2} + V_{CO})$  and  $X$  is the extent of reaction, defined as the ratio of fuel produced to the theoretical fuel productivity, as set by the initial oxygen nonstoichiometry.



<i>Cycle No.</i>	$V_{H_2} (mL g^{-1})$	$V_{CH_4} (mL g^{-1})$	$V_{CO} (mL g^{-1})$	$S_{CH_4} (%)$	$X$
1	$3.5 \pm 0.3$	$0.74 \pm 0.06$	$0.31 \pm 0.02$	44	$1.0 \pm 0.1$
6	$3.2 \pm 0.3$	$0.74 \pm 0.06$	$0.28 \pm 0.02$	46	$1.0 \pm 0.1$
11	$3.4 \pm 0.3$	$0.81 \pm 0.07$	$0.23 \pm 0.02$	47	$1.0 \pm 0.1$

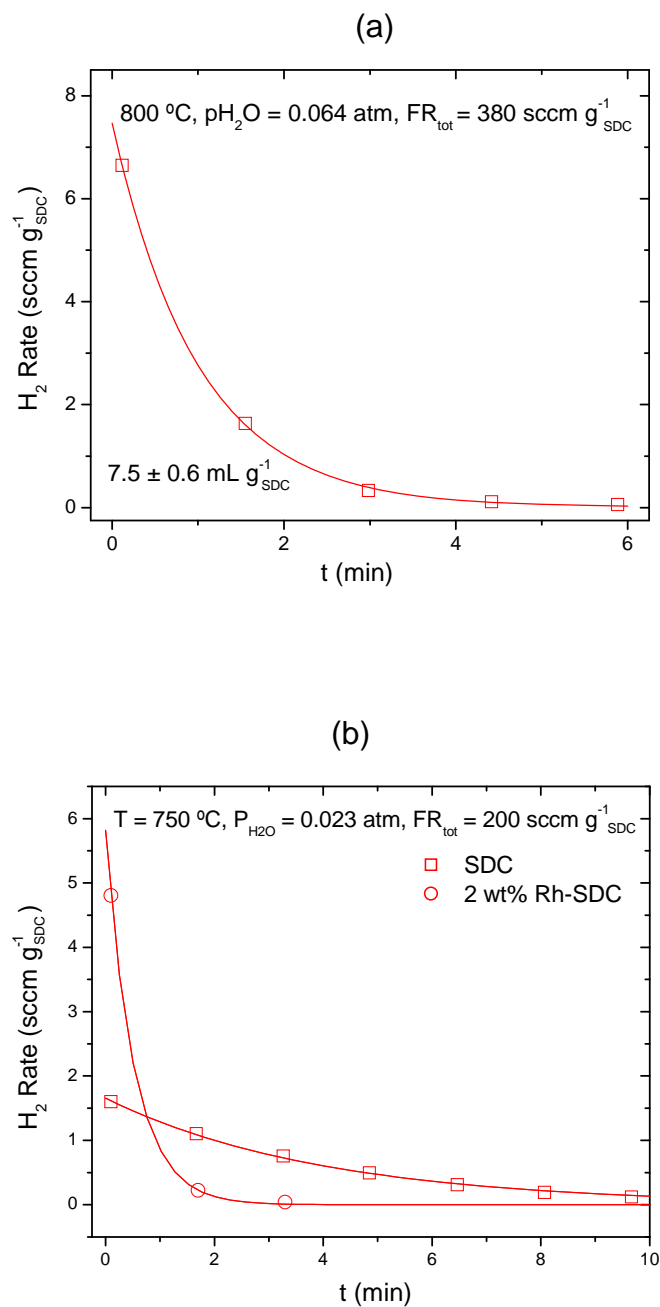
**Fig. S3 / Table S3.** Fuel production as a function of time, as measured by gas chromatography, upon simultaneous exposure of reduced Ni-SDC to H<sub>2</sub>O and CO<sub>2</sub> (balance Ar/N<sub>2</sub>) at the conditions indicated (FR<sub>tot</sub> is the total flow rate). Fuel production curves as well as CH<sub>4</sub> selectivity are stable after 11 redox cycles (other cycles at various conditions). V is the total volume of gas produced, S is the selectivity, defined as.... and X is the extent of reaction, defined as...



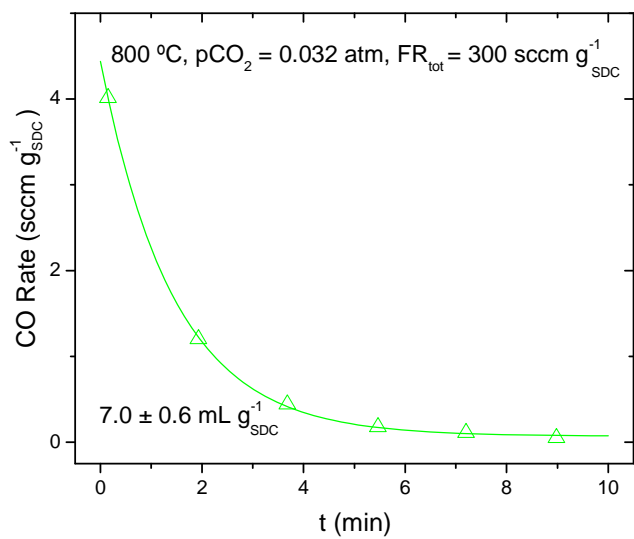
**Fig. S4.** Initial production rates of H<sub>2</sub> and CO as functions of (a) temperature and (b) reactant partial pressures when H<sub>2</sub>O and CO<sub>2</sub> are individually reacted with reduced SDC, respectively. The rates shown here correspond to that at  $t = 0$ . We take the initial state in all cases to correspond to the same value of oxygen nonstoichiometry.

The instantaneous reactant conversion rate was kept below 20 % to satisfy the gradient-less reactor and isothermal approximations ( $\Delta T < 3\text{ }^{\circ}\text{C}$ ) (Fig. S2). To avoid equilibrium limitations in the fuel production reactions, reactant flow rates were kept sufficiently high such that the  $p_{H_2O} : p_{H_2}$  and  $p_{CO_2} : p_{CO}$  ratios at the exhaust were always above 9 (for determining reaction orders) and above 5 (for determining activation energies).

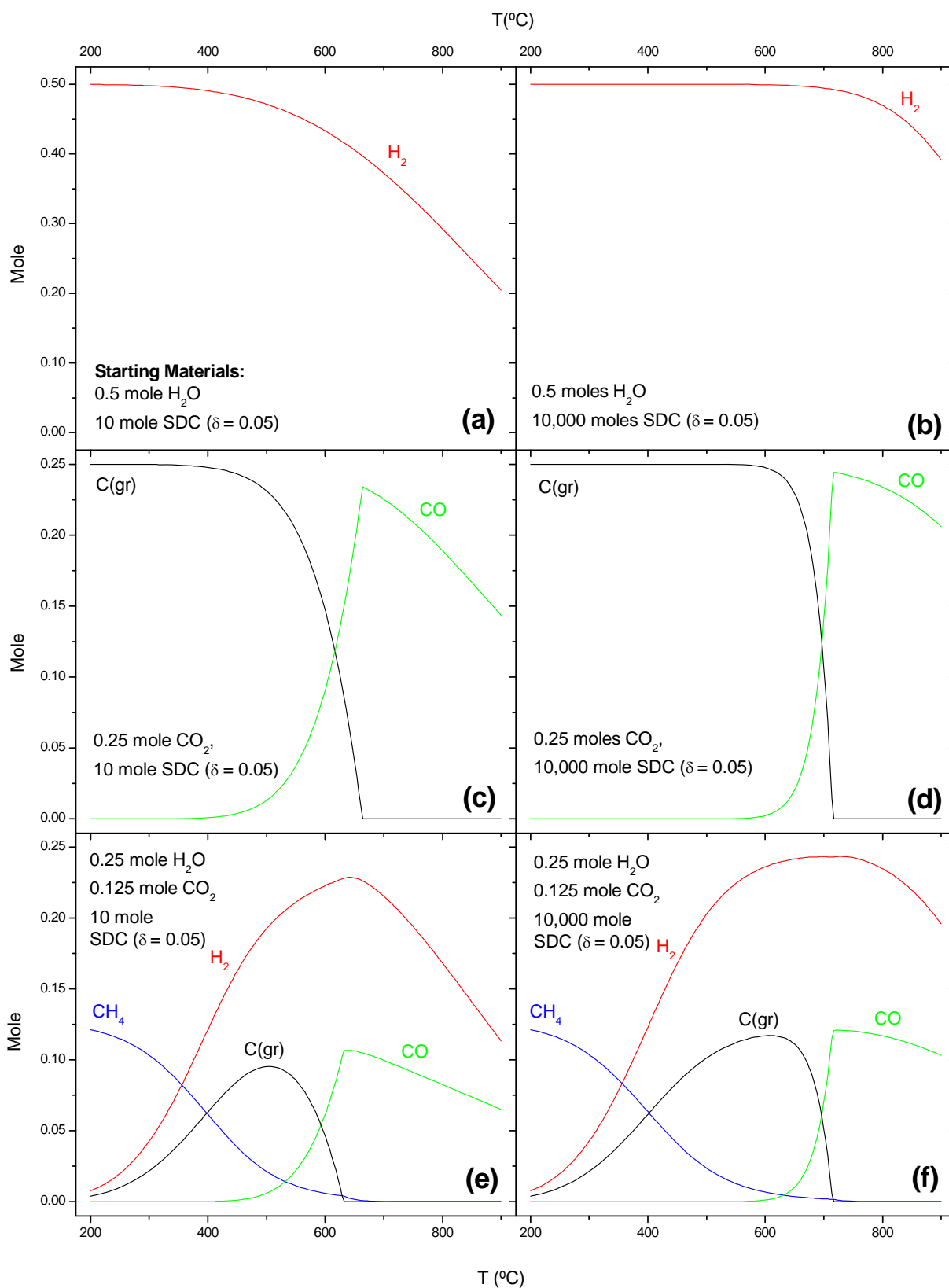




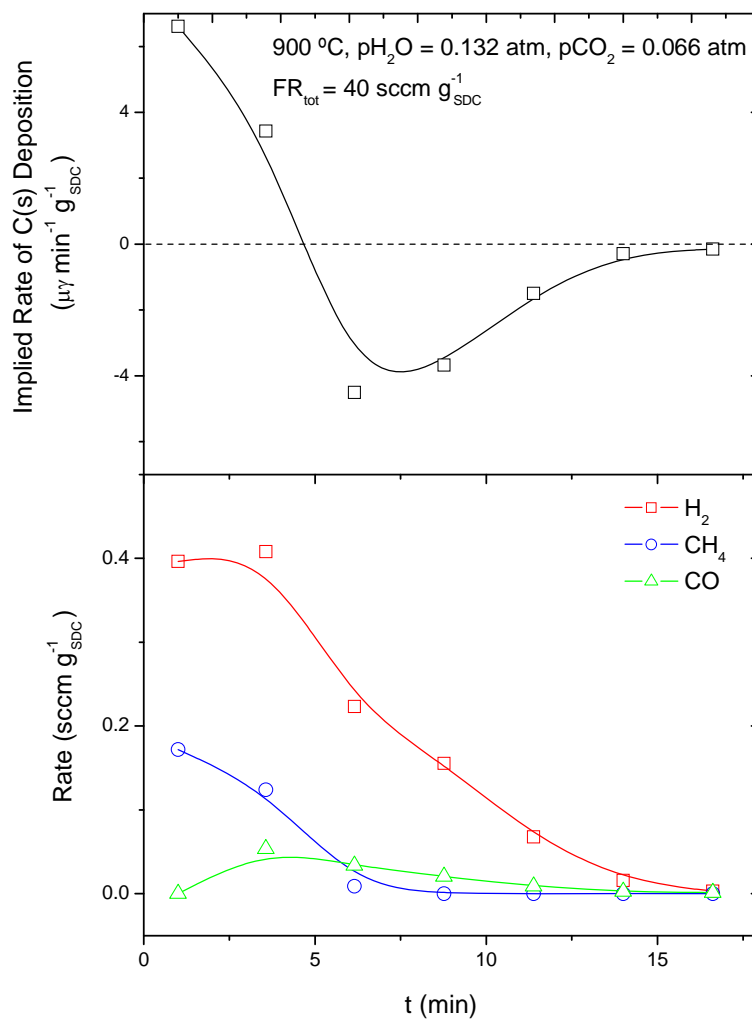
**Fig. S5.** (a)  $\text{H}_2$  production rate as a function of time, as measured by gas chromatography, upon exposure of reduced SDC to mildly humidified  $\text{N}_2/\text{Ar}$  at the conditions indicated ( $\text{FR}_{\text{tot}}$  is the total flow rate). The total quantity of hydrogen produced (value indicated) implies an extent of reaction  $X = 1.2 \pm 0.1$ . (b) Comparison of  $\text{H}_2$  fuel production curves for SDC with and without 2 wt% Rh..



**Fig. S6** CO production rate as a function of time, as measured by gas chromatography, upon reaction of CO<sub>2</sub> with reduced SDC at the conditions indicated (FR<sub>tot</sub> is the total flow rate). No C was detected as verified by post situ TPO. Total quantity of CO produced (value indicated) implies an extent of reaction of  $X = 1.1 \pm 0.1$ .



**Fig. S7.** Equilibrium compositions calculated at 1 atm for the starting materials indicated with  $p_{H_2O} = 0.064$  atm and  $p_{CO_2} = 0.032$  atm.



**Fig. S8.** (Top) Implied rate of C(s) deposition that occurs upon reaction of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  with reduced 10 wt% Ni-SDC at the conditions indicated; and (bottom) fuel production rates. Solid carbon formation rate is calculated by taking the difference between the carbon in the the product gases and that in the reactants. Integration of the carbon formation rate curve with time indicates zero carbon accumulation (within error).

<i>Process</i>	<i>Temperatures (°C)</i>	<i>Energy (kJ mol<sup>-1</sup> Syngas<sup>**</sup>)</i>
Heating oxidized SDC	800 → 1500	1431.7
Reduction of SDC (oxygen release)	1500	412.2
Cooling reduced SDC	1500 → 800	-1425.1
Cooling O <sub>2</sub> (g)	1500 → 25	-25.3
Heating H <sub>2</sub> O(l) & CO <sub>2</sub> (g)	25 → 800	122.3
Oxidation of SDC (fuel production)	800	-140.2
Cooling Excess H <sub>2</sub> O(g) & CO <sub>2</sub> (g)	800 → 25	-61.2
Cooling H <sub>2</sub> (g) & CO(g)	800 → 25	-23.3
Total energy input		1966.2
Net energy output		291.2
<b>Efficiency</b>		<b>14.8%</b>

<sup>\*\*</sup> 1 mole of syngas = 2/3 mole of H<sub>2</sub> and 1/3 mole of CO.

**Table S4.** Following a methodology reported in the literature (1-2), the cycle efficiency for syngas production from H<sub>2</sub>O and CO<sub>2</sub> using thermal energy was calculated as the ratio of the energy content of the output fuel to the various energy inputs. The oxygen release and H<sub>2</sub>O/CO<sub>2</sub> splitting half-cycle temperatures were taken to be 1500 °C and 800 °C, respectively. Ceria was assumed to attain a nonstoichiometry,  $\delta$ , of 0.05 after the reduction step, and chemical reaction was assumed to reach equilibrium.

Solar absorption efficiency (88.8 %) was determined by assuming a blackbody receiver with a solar radiation intensity of  $1 \text{ kW m}^{-2}$  and a concentration ratio of 5,000 suns in the solar concentrator. Assuming no heat recovery, a total cycle efficiency of 13.2 % is obtained. A similar result is obtained if one considers the energy content of the synthesized fuel as the net energy output. With 50 % heat recovery, the efficiency increases to 22.9 %.

Some amount of  $\text{N}_2$  with low oxygen content will be required to prevent oxidation of ceria and the product. The energy cost for  $\text{N}_2$  separation from air is typically  $\sim 20 \text{ kJ/mol}$  (3).

### **Supplementary References**

- S1. A. Steinfeld, , S. Sanders, R. Palumbo, *Energy* **1999**, 65, 43.
- S2. C. Perkins, A.W. Weimer, *Int. J. Hydrogen Energy* **2004**, 29, 1587.
- S3. H-W. Haring in *Industrial Gases Processing*, **2008**.